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**Japanese Published Unexamined (Kokai Koho) Patent Application (A) No. 63-215722, published September 8, 1988; Application No. 62-47775, filed March 4, 1987; Int. Cl.: C 08 G 73/00; Inventor(s): Mutsumi Kameyama et al; Assignee: Showa Denko K.K.; Japanese Title: Method to Manufacture Conductive Polyaniline Compound**

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## **METHOD TO MANUFACTURE CONDUCTIVE POLYANILINE COMPOUND**

### **CLAIM(S)**

**A method to manufacture a conductive polyaniline compound characterized in that an aniline compound expressed by formula (I) is polymerized in the presence of macromolecular anionic electrolyte expressed by formula II. [T. Note: Formula (I) and formula (II) are attached to the end of translation.]**

### **DETAILED DESCRIPTION OF THE INVENTION**

#### **(Field of Industrial Application)**

**The present invention pertains to a method to manufacture a conductive polyaniline compound which is heat-resistant and useful as an organic semiconductor material for electron devices, electro-chromic devices, solar batteries, secondary battery activating materials, and for solid electrolytic condensers.**

#### **(Prior Art)**

**It is well-known to produce conductive macromolecule by doping a dopant in a macromolecule substance, and particularly, detailed studies have been conducted**

on polyacetylene and polyparaphenylene. For example, it is publicly known that by doping  $\text{AsF}_5$  as an acceptor into polyacetylene or doping sodium as a donor into polyacetylene, p type or n type conductive macromolecule can be produced. Also, it is known that conductive macromolecule having the conductivity in the range of electrical insulator or semiconductor to metal region can be produced by doping various dopants into polyphenylene sulfide, polythiophene, polypyrrole, or polyaniline. It is evident that the conductivity of these macromolecules can be appropriately controlled by adjusting types of dopant and the amount to be used.

These conductive macromolecules are expected to be useful as organic semiconductor materials for solar batteries, electrodes, electro-chromic devices, and solid electrolytic condensers.

With most of the prior art conductive macromolecules, relatively low molecular anion is used as a dopant, e.g., low molecular anion, such as  $\text{BF}_4^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{ClO}_4^-$ , so the dopant is dissociated when heated to a high temperature, becoming an insulator, so they are not desirable as organic semiconductor material that requires heat-resistance.

By contrast, a method to manufacture conductive polypyrrole having macromolecular electrolyte as a dopant is proposed (Chemistry Letters, Shimizu et al., 1986, p. 687). This is a method, wherein pyrrole is polymerized by electrolysis in

**the presence of macromolecular electrolyte, e.g., polyvinyl potassium sulfate to produce the conductive pyrrol doped with macromolecular anion.**

**However, the heat-resistance of the conductive polypyrrole produced by this method is necessarily satisfactory and suffers from the problem that the dopant is dissociated at a high temperature, dramatically reducing the electrical conductivity.**

**(Problem of the Prior Art to Be Solved)**

**The objective of the present invention is to offer a method to manufacture heat-resistant conductive polyaniline compound by solving the problem of the prior art conductive macromolecule.**

**(Means to Solve the Problems)**

**The present invention presents a manufacturing method of conductive polyaniline compound that can achieve said objective. More specifically, the method of manufacturing the conductive polyaniline compound of the present invention is characterized in that an aniline compound expressed by formula (I) is polymerized in the presence of macromolecular anionic electrolyte expressed by formula (II). [T. Note: Formula (I) and formula (II) are attached to the end of the translation.]**

**The method to manufacture the conductive polyaniline compound of the present invention is explained below.**

**As representative examples of the aniline compounds expressed by the**

**formula (I) are follows: aniline; ortho- or meta-toluidine; xylidine; 2.5-dimethoxyaniline; 2.5-ethoxyaniline; 3.5-dimethoxyaniline; 2.6-dimethoxyaniline. Among these aniline compounds, aniline is preferably used. As to the aniline compound, a single component is generally polymerized, but two or more may be combinedly used if necessary.**

**As to said macromolecular anionic electrolyte expressed by said formula (II), the following can be cited: anionic polyacrylate; anionic polymetacrylate; anionic polyvinyl sulfonate; anionic polyaryl sulfonate; anionic polystyrene sulfonate; anionic polyvinyl sulfonate. In the present invention, a macromolecular electrolyte containing the above macromolecular anion or one of the above anions can be used. Or two of them may be combined for use. As to these macromolecular anionic electrolyte, the one having average mol weight 500 or more is preferred, particularly, anionic polystyrene sulfonate having average 500 or more mol weight is preferred.**

**In the method of the present invention, the aniline compound is polymerized in the presence of macromolecular anionic electrolyte.**

**The amount of the macromolecular anionic electrolyte to be used at the time of polymerizing the aniline compound is not limited to a specific amount. Generally, to the aniline compound 100 parts by weight, the macromolecular anionic electrolyte is 1-500 parts by weight, preferably 2-200 parts by weight, more preferably 4-100**

parts by weight.

To manufacture the conductive aniline compound, any method can be used, but, it is generally preferred to use a method, wherein the aniline compound is **chemically** or electrochemically polymerized in the presence of macromolecular anionic electrolyte. In the present invention, the polymerization is performed in a solvent for smooth and efficient polymerization. As a solvent, water or organic solvent is used. As to the organic solvent, acetonitrile, benzonitrile, tetrahydrofuran, and propylene carbonate can be cited. In this case, it is desirable that macromolecular anionic electrolyte is dissolved in the polymer solvent composed of aniline compound and of solvent, but the undissolved slurry also can be used.

The pH of the polymer solution composed of aniline compound, macromolecular electrolyte and of solvent is good enough as long as its pH is less than 3.9, but preferably 0.5-3.0, more preferably, 0.8-1.5.

The polymerization parameters are not limited to a specific range, but the reaction temperature preferably used is generally -20-100°C, preferably 0-80°C. Also, the reaction time is not specifically limited, 1-48 hours are generally used, but it can be selected properly in relation to the reaction temperature. In the electrochemical polymerization, a constant-current method or a constant voltage method can be used.

**(Embodiment)**

**(Embodiment Example 1)**

To the preliminarily deoxidized distilled water, aniline and polystyrene sulfonate were added to prepare an electrolytic polymer solution 200 ml. The aniline concentration in the solution was 0.4 mol and polystyrene sulfonate (approximate average mol weight 70,000) concentration was 0.45 mol. Into this solution, two platinum electrodes, each having surface dimension 6 cm<sup>2</sup>, were inserted with a 2 cm distance between them, and subsequently, 100 Coulomb current was supplied to conduct electrolytic polymerization. Then, on the anode platinum electrode, dark green polyaniline was deposited. After the electrolytic polymerization, the anode that has been coated was washed with distilled water, and vacuum-dried at 80°C. Then, the polyaniline was peeled from the platinum electrode. When the sulfur atoms in the produced dark green polyaniline was analyzed, it was found that 50 weight% of polystyrene sulfonate anion was contained in this polyaniline.

The electrical conductivity (direct current-four terminal method) of polyaniline film thus produced was  $2.2 \times 10^{-2}$  S/cm at a normal temperature,  $2.0 \times 10^{-2}$  S/cm at 100°C,  $1.1 \times 10^{-2}$  S/cm at 200°C, and  $9.7 \times 10^{-5}$  at 280°C. There was little change in electrical conductivity by the change of temperature, and the heat-

resistance was excellent.

**(Embodiment Examples 2-3)**

Except that aniline compound was used in place of aniline used in Embodiment Example 1, the same method as in Embodiment Example 1 was used for electrolytic polymerization. The pH of electrolytic polymerization solution was less than 1. The property of the produced polyaniline compound film is shown in Table 1.

	aniline compound	polystyrene sulfonate anion * (weight%)	electrical conductivity (S/cm)		
			20°C	100°C	200°C
Embodiment Example 2	2,5-dimethoxy aniline	33	$7.0 \times 10^{-3}$	$6.7 \times 10^{-3}$	$3.5 \times 10^{-5}$
Embodiment Example 3	2,6-diethoxy aniline	25	$2.4 \times 10^{-5}$	$22 \times 10^{-5}$	$1.0 \times 10^{-5}$

Note: \* indicates the amount of polystyrene sulfonate anion in polyaniline compound.

[T. Note: Assumption was made in typing in the figures in subscript for their being illegible.]

**(Comparison Example 1)**

Except that  $\text{HBF}_4$  was used in place of polystyrene sulfonate used in Embodiment Example 1, the same method as in Embodiment Example 1 was used for electrolytic polymerization. Then, polyaniline doped with 48 weight%  $\text{BF}_4^-$  was produced. The conductivity of this polyaniline was  $7.1 \times 10^{-1}$  S/cm at 20°C and  $5.7 \times 10^{-6}$  S/cm at 200°C. As the temperature rose, the electrical conductivity dropped



dramatically.

**(Comparison Example 2)**

Except that pyrrole was used in place of aniline used in Embodiment Example 1, the same method as in Embodiment Example 1 was used for electrolytic polymerization. The content of polystyrene sulfonate anion in the produced polypyrrole was 33 weight%. The electrical conductivity of this pyrrole was  $6.4 \times 10^{-1}$  S/cm at 20° and  $1.7 \times 10^{-5}$  S/cm at 200°C. As the temperature rose, the conductivity dropped dramatically.

**(Embodiment Example 4)**

Preliminarily deoxidized distilled water 400 ml was put in a three -port flask and agitated for 1 hour to bubble a nitrogen gas. Subsequently, a nitrogen gas atmosphere was created in the reaction system, and a thermometer and condenser were provided to the system. Then, the flask was cooled with water and ice water to bring the solution temperature to 15°C. Aniline 20 g and polyvinyl sulfate (approximate average mol weight 10,000) 50 g were added. The pH of the polymerization solution was less than 1. Subsequently, ammonium persulfate 22g was gradually added and agitated while the temperature was kept at 25°C or less to conduct the reaction for 5 hours. After the reaction, the greenish brown reaction solution was filtered and vacuum-dried. Thus dark green colored polyaniline 15 g

was produced. The produced dark green polyaniline was washed with 1,000 ml of distilled water, and vacuum-dried at 80°C for 15 hours.

This was washed with 1.2 - dimethoxyethane and dried at 80°C for 15 hours.

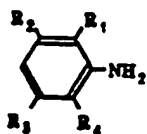
When sulfur atoms in the polyaniline powder was analyzed, it was found that 23 weight% polyvinyl sulfate anion was contained in this polyaniline.

Pressure was applied to the polyaniline powder thus produced to form a film, and the electrical conductivity (by DC four-terminal method) at a normal temperature was measured. It was  $3.8 \times 10^{-2}$  S/cm. This film was again heated and its conductivity was again measured. It was  $1.5 \times 10^{-2}$  S/cm at 200°C, and its conductivity at a normal temperature was nearly the same.

(Advantage)

The conductive polyaniline compound produced by the method of the present invention evenly contains the macromolecular anion electrolyte contained in the reaction system, and its conductivity at a normal temperature was as high as  $10^{-3}$  -  $10^2$  S/cm and was stable at a temperature as high as 280°C; therefore, it is extremely useful for industrial application as an organic semiconductor material.

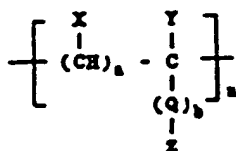
**Formula (I)**




(I)

(In the formula,  $R_1 - R_4$  may be the same or different; they refer to alkyl having 1-5 hydrogen and carbon atoms or to alkoxy having 1-10 carbon atoms.)

**Formula (II)**



(II)

(In the formula, X and Y refer to alkyl having hydrogen atoms or carbon atoms less than 10. Z indicates  $-\text{COO}^-$ ,  $-\text{OSO}_3^-$ ,  $-\text{SO}_3^-$ . a and b indicate positive integers 0 or less than 10. Q indicates methylene ( $-\text{CH}_2-$ ) or phenylene (). n indicates a positive integer higher than 3.